



## Electropolymerization of 4,4'-Methylenedianiline onto the Gold Electrode in Non-Aqueous Medium and Investigation of Electrochemical and Spectroelectrochemical Behaviours

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(Received: 27 February 2012;

Accepted: 15 May 2012)

AJC-11499

In this work, electrochemical and spectroelectrochemical behaviours of 4,4'-methylenedianiline have been studied by using cyclic voltammetry, electrochemical impedance spectroscopy and differential pulse voltammetry technique. In cyclic voltammetry surface characterization performed study, the grafting process of 4,4'-methylenedianiline on the electrode surface has been performed using 1 mM 4,4'-methylenedianiline solution in 100 mM tetrabutylammonium tetrafluoroborate in the range from 0.0 mV to +1600 mV potential range at 100 mV s<sup>-1</sup> sweeping rate with 30 cycles. The surface characterization process has been carried out by using cyclic voltammetry and electrochemical impedance spectroscopy technique in both aqueous and non-aqueous media. Differential pulse voltammetry technique has been used to support the clear binding of molecule to the electrode surface. A polymerization mechanism for the binding process has also been suggested.

**Key Words:** 4,4'-Methylenedianiline, Modified electrode, Cyclic voltammetry, Differential pulse voltammetry.

### INTRODUCTION

Electrochemical polymerization reactions on anode surfaces have been observed and studied for decades<sup>1</sup>. Electrochemical methods are based on direct oxidation or reduction of substrate onto an electrode surface. Electrode reactions are most suitable for analytical applications due to their requirements of high potential. Moreover, these surfaces can be modified by reductive substrate for analytical applications<sup>2,4</sup>.

Modified electrodes are being used frequently in the voltammetric determination of organic compounds because of their efficiency and selectivity, which can be obtained by varying the modifier<sup>5,6</sup>.

### EXPERIMENTAL

Tetrabutylammonium tetrafluoroborate, 4,4'-methylenedianiline, acetonitrile and other chemicals were obtained from Riedel de Haën (Seelze, Germany) or Sigma-Aldrich (Buchs SG, Switzerland), chemical companies and so no further purification was performed. Ultra pure quality of water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used in preparations of aqueous solutions, cleaning of the glassware and polishing the electrodes. In all experiments, the electrodes were kept in CH<sub>3</sub>CN when they were not in use. All the experiment solutions were prepared at 1 mM concentration. Solutions were thoroughly deoxygenated by purging with purified argon

gas (99.99 %) for 10 min prior to the electrochemical experiments.

Electrochemical measurements were performed with GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The working electrode was a Au electrode BAS model MF-2014 (1.6 mm dia.). The reference electrodes an Ag/Ag<sup>+</sup> (10 mM AgNO<sub>3</sub>) (BAS Model MF-2042) for non-aqueous media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used. Pt wire (BAS Model MW-1032) was used as a counter electrode.

The gold electrode (1.6 mm dia.) was prepared to remove the oxide and other functionalities by polishing first with fine wet emery papers (Buehler with grain size of 4000) and then with 1.0, 0.3 and 0.05 μm alumina slurry made from aluminum suspension solution on a Buehler polishing microcloth. After removal of trace alumina from the surface by rinsing with water and brief cleaning in ultrasonic water bath with water then an IPA + CH<sub>3</sub>CN mixture purified over activated carbon, the gold electrode was rinsed with CH<sub>3</sub>CN to remove any physisorbed and unreacted materials from the electrode surface. The gold slide (*i.e.* gold coated SF10) substrates were first cleaned by repeated rinsing with deionized water and CH<sub>3</sub>CN. They were then further cleaned with a mixture of NH<sub>3</sub> (25 %, v/v), H<sub>2</sub>O<sub>2</sub> (30 %, v/v) and ultrapure water having a volume ratio of 1:1:5 at a temperature of 70 °C for 20 min<sup>7</sup>.

## RESULTS AND DISCUSSION

The grafting of 4,4'-methylenedianiline on the electrode surface has been performed using 1 mM 4,4'-methylenedianiline solution (in 100 mM  $\text{NBu}_4\text{BF}_4$ ) in the range from 0.0 mV to +1600 mV potential range at  $100 \text{ mV s}^{-1}$  sweeping rate with 30 cycles. As can be clearly seen from Fig. 1, 4,4'-methylenedianiline molecule binds to Au electrode surface through polymerization process. The performed surface characterization studies shows that the grafted surface is more active than the bare Au surface especially in non-aqueous medium.

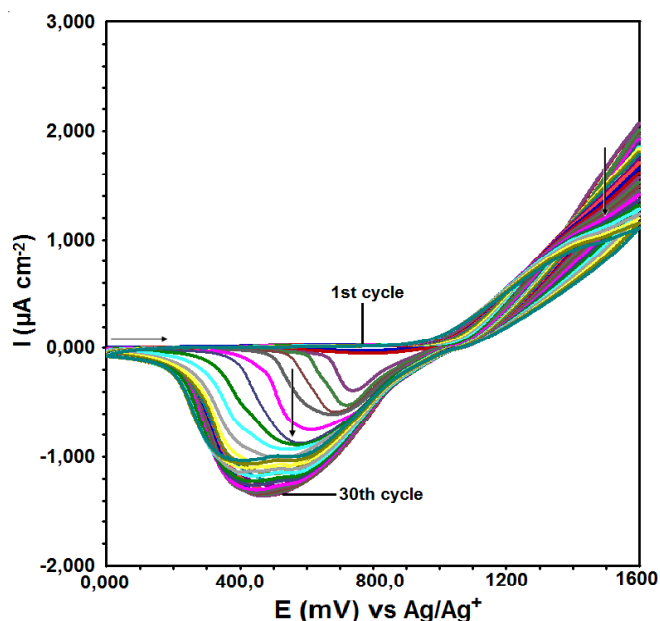


Fig. 1. Cyclic voltammogram of 4,4'-methylenedianiline vs.  $\text{Ag}/\text{Ag}^+$  (10 mM  $\text{AgNO}_3$ ) on a Au working electrode. Potential range from +0.0 mV to +1600 mV, sweep rate is  $100 \text{ mV s}^{-1}$

Surface characterizations after the modification process were carried out by cyclic voltammetry (Fig. 2) and electrochemical impedance spectroscopy (Fig. 3). In the characterizations with cyclic voltammetry, 1 mM ferrocene solution in 100 mM  $\text{NBu}_4\text{BF}_4$  was carried out in the potential range from -200 mV to +400 mV in non-aqueous medium and 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in Britton-Robinson (BR) buffer solution, pH 2, was performed in the potential range from +500 mV to -100 mV in aqueous medium at sweep rate of  $100 \text{ mV s}^{-1}$ . The surface voltammogram of 4,4'-methylenedianiline/Au electrode was compared with surface voltammogram of the bare Au electrode.

Electrochemical impedance spectroscopy is a suitable technique for investigation of surface properties. It is capable of giving useful data about defects/holes of the modified surface, the kinetics and mechanism of the surface formation processes, surface coverage and so forth<sup>8,9</sup>. This case was supported by the results of the electrochemical impedance spectroscopy obtained by using 10 mV potential and a mixture of 1 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  at 100.000 Hz and 0.05 Hz. The electrochemical impedance spectroscopy graphs obtained after modifications in non-aqueous medium of electrode surface are given in Fig. 3.

According to the data obtained from the characterization procedures, an interpretation was done over the fact that 4,4'-

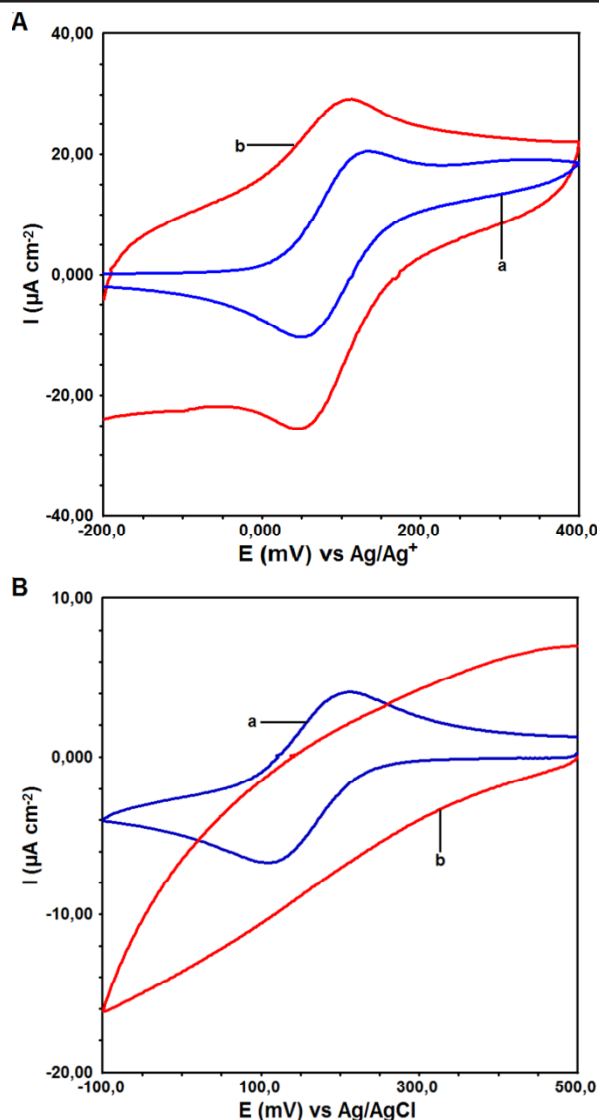


Fig. 2. Overlying cyclic voltammograms for (A) 1 mM ferrocene redox probe solution vs.  $\text{Ag}/\text{Ag}^+$  (10 mM  $\text{AgNO}_3$ ) in  $\text{CH}_3\text{CN}$  containing 100 mM  $\text{NBu}_4\text{BF}_4$ ; (B) 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  redox probe solution vs.  $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$  reference electrode in BR buffer solution, pH=2, with a Au working electrode at  $100 \text{ mV s}^{-1}$  sweep rate (a, bare Au; b, 4,4'-methylenedianiline/Au)

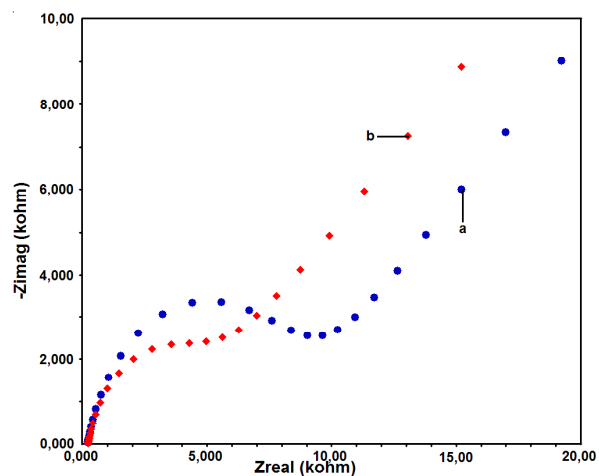
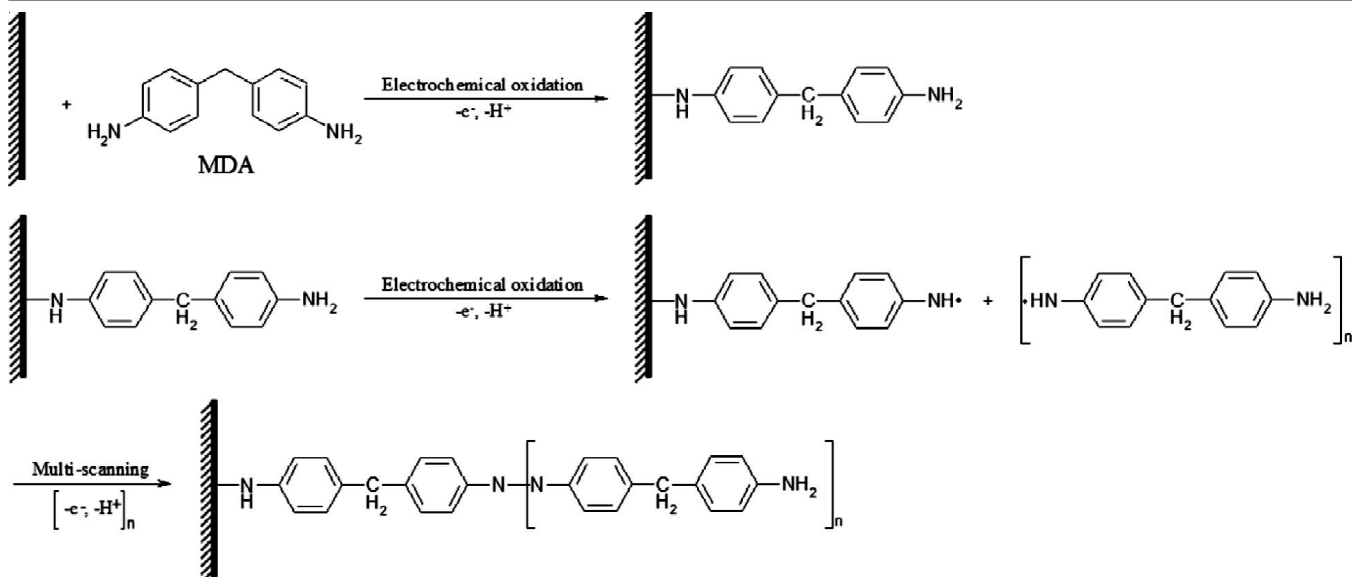


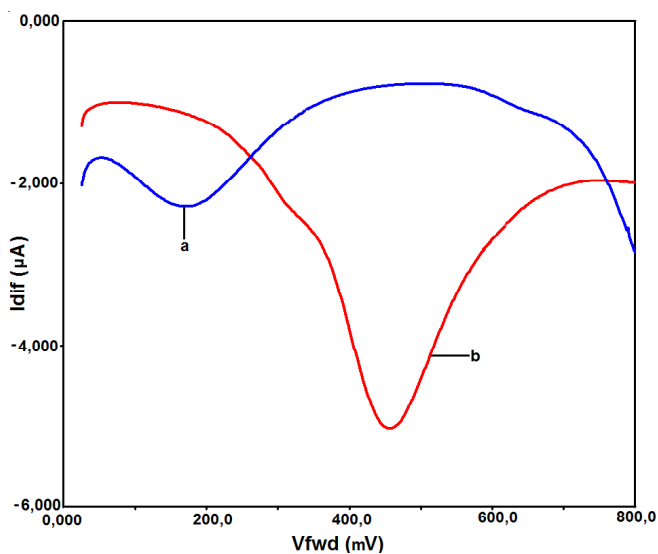
Fig. 3. Nyquist plots for electrochemical impedance spectra of 1 mM  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox couple solution in 100 mM KCl at the frequency range of 100.000-0.05 Hz at 10 mV wave amplitude, on a Au working electrode (a, bare Au; b, 4,4'-methylenedianiline/Au)



**Scheme-I:** Modification mechanism of 4,4'-methylenedianiline at Au electrode surface (in MeCN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub>)

methylenedianiline molecules in non-aqueous media are grafted on the GC electrode surfaces. Electrochemical impedance spectroscopy is a valuable method to monitor the impedance changes of the electrode surface during the modification process. The semicircle diameters of Nyquist plot reflects the electron transfer resistance (Ret), which is from the electron transfer of the redox probe Fe(CN)<sub>6</sub><sup>3-</sup>/Fe(CN)<sub>6</sub><sup>4+</sup> solution.

Differential pulse voltammetry technique has been used to support the clear binding of molecule to the electrode surface. In differential pulse voltammetry experiments, the potential range was from 0.0 mV to +1000 mV, the potential scan rate was 50 mV s<sup>-1</sup>, the pulse amplitude was 25 mV, the pulse period was 0.05 s and the sample period was 1.0 s. The differential pulse voltammogram of the modified electrode was compared with the differential pulse voltammogram of bare Au electrode (Fig. 4).



**Fig. 4.** Differential pulse voltammeters (sweep rate 25 mV s<sup>-1</sup>) of 1 mM 4,4'-methylenedianiline in CH<sub>3</sub>CN containing 100 mM NBu<sub>4</sub>BF<sub>4</sub> vs. Ag/Ag<sup>+</sup>/(10 mM AgNO<sub>3</sub>) on a Au working electrode (a, bare Au; b, 4,4'-methylenedianiline/Au)

The suggested reaction mechanism is given in **Scheme-I**. The article by Isbir-Turan *et al.*<sup>2</sup> was used as a supporting reference for the suggested mechanism. As it can be figured out from Fig. 1, 4,4'-methylenedianiline molecule binds to the electrode surface through C-N covalent bond over -NH<sub>2</sub> group losing 1e<sup>-</sup> and 1H<sup>+</sup>. An electroactive polymer surface was obtained.

## Conclusion

By the use of 4,4'-methylenedianiline for the modification of Au electrode, an electroactive polymer surface was obtained in this study. Modification process has been carried out by using cyclic voltammetry and surface characterization process has been done by using cyclic voltammetry and electrochemical impedance spectroscopy. Differential pulse voltammetry technique has been used to support the data obtained from the electrochemical and spectroelectrochemical studies. The following step of this research will be the use of this developed electrode as a chemical sensor electrode for the quantitative determination of polyphenolic molecules in different media.

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